Redistillation of a portion (197 g.) of the first fraction provided three fractions: (1) 61 g., b.p. 53–55°; (2) 92 g., b.p. 55–58°; (3) 28 g., b.p. 58–59°. All three fractions had a pronounced odor of isobutyraldehyde. A portion of fraction 2 was characterized as its 2,4-dinitrophenylhydrazone (m.p. 184–184.5°) and its melting point was not depressed when mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of isobutyraldehyde.

A portion (72 g.) of the steam-distilled fraction was redistilled to provide 22 g. of a fore-fraction consisting mainly of the water–crotonaldehyde azeotrope, 38 g. of refined crotonaldehyde boiling at 99–101° and 11 g. of viscous residue. The 2,4-dinitrophenylhydrazone of the refined material melted at 191–192.5° after one recrystallization from a mixture of ethanol and ethyl acetate. The melting point of this material was not depressed when mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of crotonaldehyde.

De-alcoholation of 3-Butoxy-4-hexenal.—A mixture of 128 g. (0.75 mole) of 3-butoxy-4-hexenal, 300 ml. of water and 0.34 ml. of concentrated sulfuric acid was heated at the reflux temperature for 2.5 hours. An additional 0.66 ml. of sulfuric acid was added and the mixture heated for 3 hours longer. After cooling the mixture, the water layer was removed, neutralized with sodium bicarbonate and extracted 3 times with 100-ml. portions of diethyl ether. The extracts and the organic layer were combined and distilled. After distilling off the ether, there were obtained 5 fractions: fract. 1, 20 g., b.p. 56–57° (50 mm.); fract. 2, 8 g., b.p. 56 to 52° (50 to 10 mm.); fract. 3, 32 g., 52–53° (10 mm.); fract. 4, 8 g., 53 to 86° (10 mm.); fract. 5, 29 g., 86–88° (10 mm.).

Fraction 1 contained in excess of 95% 1-butanol, little or no secondary butanol and a small amount of an unknown, high-boiling material which may have been 2,4-hexadienal. These values were determined by mass spectroscopy. Fraction 3 was 2,4-hexadienal and fraction 5 was recovered 3-butoxy-4-hexenal.

2-Ethyl-2,4,6-octatrienal.—The residue (575 g.) from the reaction of 9 moles of 2,4-hexadienal and 3 moles of 1-butenyl ethyl ether, from which the unreacted hexadienal had been removed, was mixed with 575 g. of 50% aqueous acetic acid containing 1 ml. of concentrated sulfuric acid. The mixture was heated at the reflux temperature on a still and 128 g. of a mixture of ethanol and ethyl acetate was removed by distillation. The residue was cooled and the sulfuric acid neutralized with a solution of 1.5 g. of sodium hydroxide in 100 ml. of water. The organic layer was removed and washed once with 250 ml. of water. Distillation of the organic material provided 209 g. of crude 2-ethyl-2,4,6-octatrienal, b.p. 77–94° (1 to 2 mm.). This product was identified by hydrogenation in 250 ml. of ethanol solvent in the presence of 20 g. of Raney nickel catalyst at 150 p.s.i.g. There was obtained 175 g. (81% yield, assuming 100% pure 2-ethyl-2,4,6-octatrienal starting material) of 2-ethyloctanol, b.p. 104–105° (10 mm.), n^{20}D 1.4379. The allophanate of

2-ethyloctanol was prepared[12] and after three recrystallizations from ethanol–water melted at 111–111.5°.

Anal. Calcd. for $C_{12}H_{24}N_2O_3$: C, 58.99; H, 9.90; N, 11.47. Found: C, 58.99; H, 9.93; N, 11.40.

C. Derivatives of 3-Ethoxy-4-hexenal.—3-Ethoxy-4-hexen-1-ol was prepared by the lithium aluminum hydride reduction of 3-ethoxy-4-hexenal using the procedure of Nystrom and Brown.[13] The reactant quantities were 142 g. (1.0 mole) of 3-ethoxy-4-hexenal, 16 g. (0.42 mole) of lithium aluminum hydride and 700 ml. of diethyl ether. The product (115 g., 80% yield) distilled at 85–86° (10 mm.), n^{20}D 1.4417.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.61; H, 11.17; unsaturation, 13.89 meq./g. (bromination). Found: C, 66.20; H, 11.20; unsaturation, 13.72 meq./g. (bromination).

The allophanate of this alcohol melted at 128.5–129.5° after two recrystallizations from water.

Anal. Calcd. for $C_{10}H_{18}O_4N_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.18; H, 7.85; N, 12.25.

3-Ethoxy-1-hexanol.—Hydrogenation of 504 g. (3.5 moles) of 3-ethoxy-4-hexenal at 125° and 500 p.s.i.g. over 25 g. of Raney nickel gave 392 g. of 3-ethoxy-1-hexanol (76% yield), b.p. 89–90° (10 mm.), n^{20}D 1.4262. The allophanate of this alcohol melted at 137.5–138° and its melting point was not depressed when mixed with the allophanate of an authentic sample of 3-ethoxy-1-hexanol.[14]

Anal. Calcd. for $C_{10}H_{20}O_4N_2$: C, 51.71; H, 8.68; N, 12.06. Found: C, 51.96; H, 8.22; N, 12.28.

2,4-Dinitrophenylhydrazones.—The preparation of the 2,4-dinitrophenylhydrazones of the β-alkoxyaldehyde products by standard techniques[15] always resulted in partial and sometimes complete de-alcoholation of the aldehyde. The resulting products proved difficult to purify or were completely converted to the derivative of the α,β-unsaturated aldehyde. The hydrazones were prepared by the procedure which follows for 3-ethoxy-4-hexenal. To a hot solution of 1.6 g. of 2,4-dinitrophenylhydrazine and 300 ml. of methanol was added 2 g. of 3-ethoxy-4-hexenal and 75 ml. of water. The product crystallized on standing to give long, yellow needles which were recrystallized three times from heptane; m.p. 103.5–104°. In some instances the formation of the derivative was facilitated by the addition of a drop or two of concentrated phosphoric acid.

(12) A. Behal, *Bull. soc. chim. France*, [4] **25**, 473 (1919).

(13) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

(14) 3-Ethoxy-1-hexanol was prepared by the reaction of diethyl butyral and vinyl ethyl ether² followed by hydrolysis of the 1,1,3-triethoxyhexane to 3-ethoxyhexanal which was catalytically hydrogenated.

(15) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

SOUTH CHARLESTON, W. VA.

Unsaturated Phenols. V. The Reaction of Isoprene with Phenol[1]

BY ALFRED R. BADER AND WILLIAM C. BEAN

The reaction of isoprene with phenol, catalyzed by phosphoric acid, yields the o- and p-3-methylcrotylphenols IV and V, the γ-hydroxyisoamylphenols II and VIII, and the two chromans I and IX.
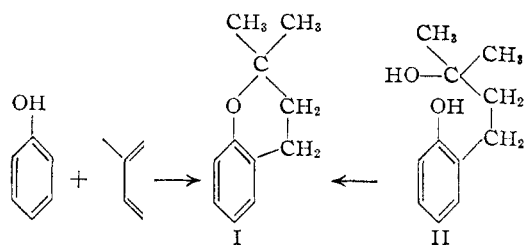
The reactions of isoprene with phenol have been studied briefly by Claisen[2] and by Pines and Vesely.[3] Claisen obtained 2,2-dimethylchroman (I) which proved identical with the ether synthesized by ring closure of the tertiary alcohol II prepared by

(1) For paper IV, see THIS JOURNAL, **79**, 6164 (1957).

(2) L. Claisen, *Ber.*, **54B**, 200 (1921); German Patent 374,142 (Dec., 1920).

(3) H. Pines and J. A. Vesely, U. S. Patents 2,553,470 and 2,578,206 (May and Dec., 1951).

the action of methylmagnesium iodide on ethyl dihydrocoumarate. Pines and Vesely, who used the alcohol and ether complexes of stannic chloride, and the ether complex of 85% phosphoric acid to prepare pentenylphenols, considered condensation to take place between phenol and the tertiary double bond of isoprene, but beyond that did not elaborate on the structures of the alkenylphenols formed. In the alkylation of phenol by the reso-

nant carbonium ion III one would *a priori* consider IV, V, VI and VII as possible products. However, alkenylations with butadiene,[1,4-6] isoprene[5,7,8] and
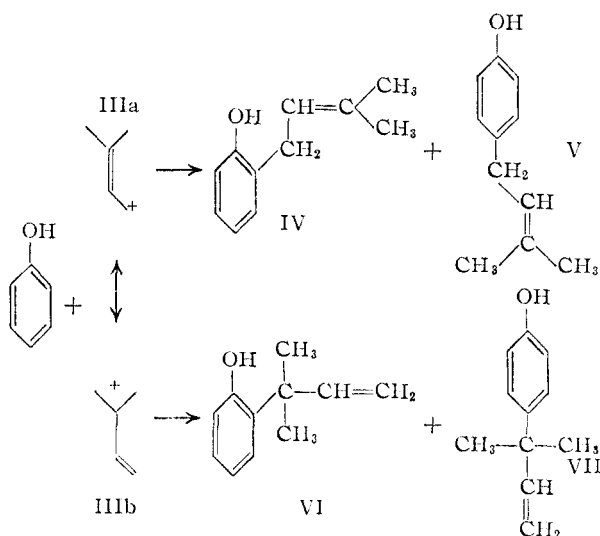
2,3-dimethylbutadiene[7] have shown that the products from the alkenylations with conjugated dienes are derived from that resonance hybrid of the carbonium ion which is *spatially most accessible;* compounds containing the crotyl, 3-methylcrotyl and 2,3-dimethylcrotyl groups are the predominant products in the alkenylations with butadiene, isoprene and 2,3-dimethylbutadiene respectively.

From the reaction of phenol with isoprene catalyzed by 71% phosphoric acid[9] at 20°, we obtained six products. The phenolic fraction yielded the 3-methylcrotylphenols IV and V and the crystalline tertiary alcohols II and VIII: the ethereal fraction consisted of 2,2-dimethylchroman I and an alcohol IX, $C_{16}H_{24}O_2$, melting at 51–52°.

That the pentenylphenols $C_{11}H_{14}O$ have structures IV and V rather than VI and VII was proved by (i) the hydrogenation of V to a *p*-amylphenol, m.p. 27–29°, different from the known *p-t*-amylphenol[10] melting at 94–95°; (ii) the infrared spectra of IV and V which did not contain bands at 910 and 990 cm.$^{-1}$ characteristic of —CH=CH$_2$[11];

(4) L. I. Smith and J. A. King, THIS JOURNAL, **63**, 1887 (1941).

(5) H. Pines, B. Kvetinskas, J. A. Vesely and E. Baclawski, *ibid.*, **73**, 5173 (1951).

(6) W. Proell, *J. Org. Chem.*, **16**, 178 (1951).

(7) L. F. Fieser, W. P. Campbell, E. M. Fry and M. D. Gates, THIS JOURNAL, **61**, 2559, 3216 (1939).

(8) L. I. Smith, H. W. Ungnade, H. H. Hoehn and S. Wawzonek, *J. Org. Chem.*, **4**, 311 (1939).

(9) For a method to determine the most convenient catalyst concentration by means of Hammett indicators, cf. paper IV.

(10) R. C. Huston and T. Y. Hsieh, THIS JOURNAL, **58**, 439 (1936).

(11) H. W. Thompson and D. H. Whiffen, *J. Chem. Soc.*, 1412 (1948).

and (iii) the alkali isomerizations[12] of IV and V to the corresponding conjugated phenols. Compounds such as VI and VII would not be expected to isomerize in alkali.
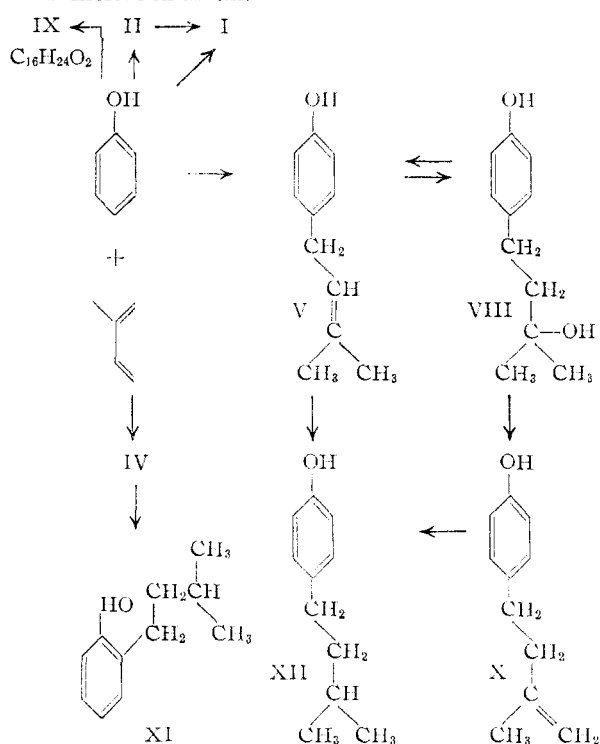
The 3-methylcrotylphenols IV and V prepared in these alkenylations could not be obtained crystalline. The *p*-isomer V, however, was easily characterized by its 2,6-bishydroxymethyl derivative, m.p. 110–111°, and the reaction of *p*-substituted phenols with formaldehyde appears to be one of the easiest means of characterization. Table I lists a number of similar dimethylol derivatives prepared. When V was treated with methanolic potassium hydroxide under the relatively mild conditions required to isomerize *o*-allyl- to *o*-propenylphenol, V remained non-conjugated, but the quite homogeneous phenol recovered crystallized easily, melted at 9–11°, and was characterized by the same bishydroxymethyl derivative melting at 110–111°. Apparently V is accompanied in the alkenylation by small amounts of an isomeric product, perhaps X, which prevents the crystallization of V, and which becomes isomerized to V in alkali.

The crystalline alcohol VIII, m.p. 134–135°, can be prepared also by the hydration of V, and is isolated particularly easily from the other products of the alkenylation because it is the only product sparingly soluble in toluene. The *o*-isomer II, m.p. 112°, had been prepared previously by Claisen[2]; its identity was proved by cyclization to I.

The dehydration of VIII yields one of two products, depending on conditions. In the presence of acid or iodine the predominant product is V characterized by its spectrum and bishydroxymethyl derivative. When, however, VIII is heated at atmospheric pressure without catalysts, dehy-

(12) A. R. Bader, THIS JOURNAL, **78**, 1709 (1956).

dration also occurs to a pentenylphenol melting at 9–12°. This product, however, depresses the m.p. of V, shows in the infrared a strong band at ca. 11.3 μ absent in the spectrum of V and characteristic of a double bond $RR'C=CH_2$,[11] cannot be characterized by a crystalline bishydroxymethyl derivative, and is assigned structure X.

The unsaturated phenols IV, V and X are easily hydrogenated to the isoamylphenols XI and XII melting at 12–14° and 27–29°, respectively. Such alkylphenols containing α-methylene groups are difficult to prepare by Friedel–Crafts reactions with alcohols, halides or alkenes, but are made conveniently by hydrogenation of the products of alkenylations with dienes.

The ether IX, $C_{16}H_{24}O_2$, is dehydrated easily either by heat or with 85% phosphoric acid at 25°,
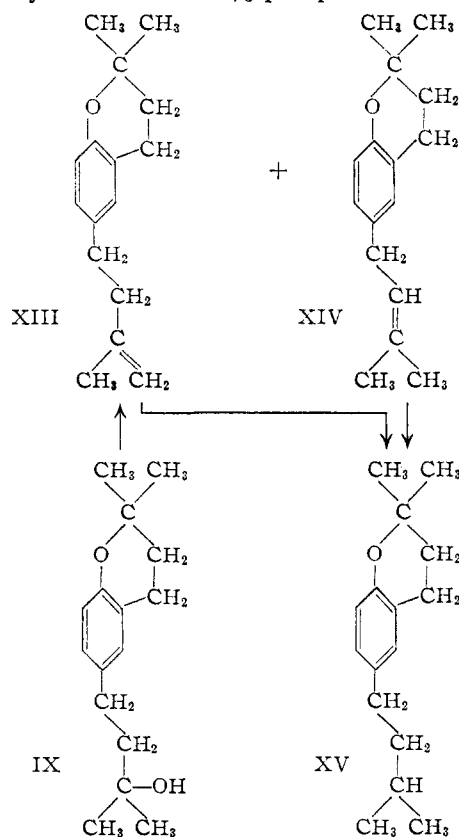
to yield the unsaturated ether XIII perhaps accompanied by some XIV. The infrared spectrum of IX in carbon disulfide shows a hydroxyl band at ca. 2.8 μ and a strong band at 12.2 μ characteristic of a substituted benzene ring bearing two adjacent hydrogen atoms. The spectrum of the dehydration product shows besides the band at 12.2 μ also a strong band at 11.25 μ characteristic of disubstituted terminal unsaturation. Hydrogenation of the unsaturated ether yields the chroman XV melting at 19–20°.

Experimental

Reaction of Isoprene with Phenol.—Preliminary experiments showed that 71% aqueous phosphoric acid corresponds in catalyst strength to the complexes used by Pines and Vesely,[3] and yields the same products. A cooled mixture of 125 g. (1.3 moles) of phenol, 90 g. (1.3 moles) of isoprene, 230 g. of toluene and 130 g. of 71% aqueous phos-

phoric acid was stirred at 20° for 16 hours. The reaction was somewhat exothermic. The reaction mixture was washed with water, and the toluene was distilled off in vacuo, leaving 212 g. of a faintly yellow oil. This mixture (200 g.) was stirred with aqueous potassium hydroxide solution to separate ethers from phenols. The ethers (24 g.) were fractionally distilled to yield 10 g. of 2,2-dimethylchroman (I),[2] b.p. 224–226°, $n^{25}D$ 1.524, and 10 g. of IX, b.p. 150–152° (0.8 mm.), $n^{25}D$ 1.523; this crystallized slowly on standing and melts at 51–52°; λ_{max}^{EtOH} 220 mμ (log ϵ 3.92), 225 mμ (infl., log ϵ 3.89), 282 mμ (log ϵ 3.40), 291 mμ (log ϵ 3.34); λ_{min} 247.5 mμ (log ϵ 2.32), 289 mμ (log ϵ 3.32).

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.45; H, 9.82.

The phenolic fraction was distilled through a Stedman column to yield 28 g. of phenol; 23 g. of a fraction, b.p. 89–91° (1 mm.), $n^{25}D$ 1.538, largely o-3-methylcrotylphenol (IV); 3 g. of a mixture of IV and V; 40 g. of a fraction b.p. 104–105° at 1 mm., $n^{25}D$ 1.539, largely p-3-methylcrotylphenol (V)[13]; and 60 g. of yellow flask residue A; λ_{max}[14] of IV 275 mμ (log ϵ 3.36), λ_{min} 242.5 mμ (log ϵ 2.10); λ_{max} of V 225 mμ (log ϵ 3.96), 279 mμ (log ϵ 3.30); λ_{min} 219 mμ (log ϵ 3.91), 247.5 mμ (log ϵ 2.19).

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.69. Found: IV: C, 81.50; H, 8.97. Found V: C, 81.05; H, 8.36.

The infrared spectrum of IV in CS_2 shows a strong band at 13.3 μ characteristic of o-substitution and absent in the spectrum of V which shows a strong band at 12.2 μ characteristic of p-substitution and absent in the spectrum of IV. The spectrum of the fraction b.p. 104–105° at 1 mm. (largely V) showed a weak band at ca. 11.3 μ. When 30 g. of this fraction was refluxed with 30 g. of potassium hydroxide in methanol at 110° for six hours, no conjugation[12] had occurred, and the recovered phenol's b.p., refractive index and ultraviolet spectrum were identical with those of the starting material. Except for the disappearance of the weak band at ca. 11.3 μ, the infrared spectra were also identical. While the alkali-untreated p-substituted phenol could not be obtained crystalline, the product recovered from this alkali treatment crystallized in the ice-box and melted at 9–11°.

The p-3-methylcrotylphenol (V) (before and after the six-hour treatment with alkali) as well as other p-substituted phenols were characterized by their 2,6-bishydroxymethyl derivatives. These are listed in Table I. A mixture of 4 g. of the phenol, 250 mg. of sodium hydroxide, 0.4 cc. of water and 4 g. of 37% formalin solution was let stand for 2 days. Toluene (10 cc.) and glacial acetic acid (3 cc.) were then added, the mixture was cooled thoroughly, and the crystalline product filtered and recrystallized.

A solution of flask residue A in toluene (200 ml.) was cooled, and the white solid, p-(γ-hydroxyisoamyl)-phenol (VIII) (12 g., m.p. 127–130°) was filtered and crystallized twice from xylene to yield 10 g. of flat needles, m.p. 134–135°; λ_{max} 224 mμ (log ϵ 3.83), 279 mμ (log ϵ 3.22); λ_{min} 245 mμ (log ϵ 1.68).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.48; H, 9.11.

The infrared spectrum of VIII in Nujol showed it to be p-substituted. It was characterized by a phenoxyacetic acid which, crystallized from water, melts at 101–102°.

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.80; H, 7.71.

The alcohol VIII can be obtained simply by diluting the initial reaction mixture with toluene (1:10) and filtering the almost pure VIII which crystallizes on standing.

The mother liquor from VIII was distilled in vacuo. The fraction, 30 g., b.p. 145–175° (0.8 mm.), crystallized partially on standing and after four crystallizations from heptane and ethanol yielded 7 g. of o-(γ-hydroxyisoamyl)-

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(13) In one experiment, W. C. B. obtained a crystalline p-substituted pentenylphenol, $C_{11}H_{14}O$ (*Anal.* Found: C, 81.52; H, 8.77) melting after one crystallization from heptane at 86°. Despite many attempts, we were not able to obtain this product again. The infrared spectrum of the compound (2% soln. in CS_2) showed between 10 and 13μ strong bands at 11.05, 11.55, 11.8, 12.25 and 12.45 μ; λ_{max} 217.5 mμ (log ϵ 3.75), 222.5 mμ (infl., log ϵ 3.71), 282.5 mμ (log ϵ 3.48); λ_{min} 245 mμ (log ϵ 2.02).

(14) Unless noted otherwise, the solvent in all ultraviolet spectrum determinations was 0.1% acetic acid in ethanol.

TABLE I
2,6-BISHYDROXYMETHYL DERIVATIVES

p-Substituent	Solvent of crystn.	M.p., °C.	Formula	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
2-Cyclopentenyl	Toluene	106	$C_{13}H_{16}O_3$	70.89	71.18	7.32	7.56
Crotyl	Aq. methanol	77–78	$C_{12}H_{16}O_3$	69.20	68.84	7.93	7.57
3-Methylcrotyl	Aq. methanol	110–111	$C_{13}H_{18}O_3$	70.24	70.44	8.16	8.27
Isoamyl	Aq. methanol	73–74	$C_{13}H_{20}O_3$	69.61	69.85	8.99	9.13
Crotyl allyl ether[a]	Toluene–heptane	80–81	$C_{15}H_{20}O_3$	72.55	72.59	8.12	8.27

[a] Made by the reaction of the sodium salt of 2,6-bishydroxymethyl-4-crotylphenol with allyl chloride.

phenol (II), m.p. 111–112°, which was characterized by cyclization to I;[2] λ_{max}^{15} 274 mμ (log ϵ 3.35), 279 mμ (infl. log ϵ 3.32); λ_{min} 242.5 mμ (log ϵ 3.20).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.06; H, 9.09.

Hydrogenation of V (Adams platinum oxide catalyst, methanol, 80°) quantitatively yielded p-isoamylphenol (XII),[16] b.p. 103–105° (1 mm.), $n^{25}D$ 1.514, which crystallized in the ice-box, m.p. 27–29°.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 79.99; H, 10.19.

Similar hydrogenation of IV yielded o-isoamylphenol (XI), b.p. 85–86° (0.5 mm.), $n^{25}D$ 1.510, which crystallized in the ice-box, m.p. 12–14°.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.03; H, 10.10.

The phenol XI was characterized by a p-nitrophenylurethan which was crystallized from a mixture of heptane and toluene and melts at 90–92°.

Anal. Calcd. for $C_{18}H_{20}N_2O_4$: N, 8.53. Found: N, 8.83.

Hydration of V.—Stirring a heptane solution of V with 80% aqueous phosphoric acid at 25° for 4 hours gave a 90% yield of VIII.

Dehydration of VIII.—A mixture of 20 g. of VIII, 400 cc. of xylene and 1 cc. of 85% phosphoric acid was refluxed with water take-off under nitrogen for one hour. The mixture was washed with water and distilled *in vacuo* to yield 16 g. of a phenol, b.p. 101–103° (0.7 mm.), the infrared and ultraviolet spectra of which indicated it to be largely V with some X. This dehydration product was characterized by its 2,6-bishydroxymethyl derivative which melted at 109–110° after several crystallizations, and which did not depress the m.p. of the derivative of pure V.

The tertiary alcohol can also be dehydrated by refluxing its xylene solutions with iodine. A solution of 5 g. of VIII and 50 mg. of iodine in 100 cc. of xylene yielded, after refluxing with water take-off for 6 hours, 1.9 g. of unreacted VIII and 2.1 g. of unsaturated phenol, largely V. With 100 mg. of iodine, there was no unreacted VIII, 2.7 g. of crude V and 1.7 g. of higher boiling products. With larger quantities of iodine, more polymeric products and some conjugated phenols are obtained.

The dehydration of VIII also can be effected simply by refluxing or slow distillation in the absence of catalysts. The product X a colorless liquid, b.p. 107–110° (1.5 mm.), $n^{25}D$ 1.537, crystallizes in the cold, melts at 9–12° and depresses the m.p. of pure V. Hydrogenation of X also yielded XII. It does not form a crystalline 2,6-bishydroxymethyl derivative, and its infrared spectrum in CS_2 shows a strong band at *ca.* 11.3 μ absent in the spectrum of V.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.69. Found: C, 81.04; H, 8.70.

The Dehydration of IX.—Twenty grams of IX was refluxed under nitrogen for 3 hours, and distilled to yield some water and 16 g. of a colorless liquid, XIII perhaps with some XIV, b.p. 112–115° (0.5 mm.), $n^{25}D$ 1.525.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.60. Found: C, 83.07; H, 9.65.

Dehydration to the same product also can be effected by stirring a solution of IX in heptane with 85% phosphoric acid at 25°. Dehydration also takes place when a xylene solution of IX is refluxed with a small amount of 85% phosphoric acid. A molecular rearrangement must take place, however, as the product has a higher refractive index and a substantially different infrared spectrum. Also hydrogenation does not yield the crystalline chroman XV.

6-Isoamyl-2,2-dimethylchroman (XV).—Hydrogenation (Adams platinum oxide catalyst, methanol, 80°) of the unsaturated ether prepared by refluxing IX, or by treating it with phosphoric acid at 25°, yields a colorless liquid, b.p. 119–120° (1.7 mm.), $n^{25}D$ 1.510, which crystallizes on cooling and melts at 19–20°.

Anal. Calcd. for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.50; H, 10.31.

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(15) The maxima at 224–225 mμ present in the spectra of V and VIII are absent in the spectra of the o-substituted II and IV.

(16) Z. M. Nazarova, *J. Gen. Chem. U.S.S.R.*, **8**, 1336 (1938); *C. A.*, **33**, 4214 (1939) gives b.p. 245–250°, $n^{27}D$ 1.505.

The Relative Rates of Side-chain Ethylation of Aromatic Hydrocarbons[1,2]

BY HERMAN PINES AND LUKE SCHAAP[3]

The relative rates of side-chain ethylation of various alkylarenes in the presence of sodium–anthracene catalyst was determined by means of competitive reactions. The relative order of ethylation is: for toluene 1.0, ethylbenzene 2.8, n-propylbenzene 1.9, and sec-butylbenzene 0.57. The relative rate of ethylation of indan is 1.35 as compared to that of toluene. Ethylation of xylenes decreases in rate in going from o-xylene to m-xylene to p-xylene. *Para* compounds in general show low rates of ethylation. p-Ethyltoluene, p-cymene and p-ethylcumene were ethylated in the presence of sodium–anthracene and potassium–anthracene catalyst. In the presence of sodium the larger alkyl groups ethylate preferentially.

The base-catalyzed side chain ethylation of aromatic hydrocarbons has been reported in several articles in recent years.[4] The ethylation products

(1) Paper XIII of the series of Base-catalyzed Reactions. For paper XII, H. Pines and W. O. Haag, *J. Org. Chem.*, **23**, 328 (1958).

(2) Taken in part from a dissertation submitted by L. Schaap in partial fulfillment of the requirements for the Ph.D. degree, August, 1957.

(3) Predoctoral fellow Universal Oil Products Co., 1954–1955, 1956–1957; Standard Oil Co. (Indiana), 1955–1956.

(4) (a) H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 554 (1955); (b) H. Hart, *ibid.*, **78**, 2619 (1956); (c) S. E. Voltz, *J. Org. Chem.*, **22**, 48 (1957); (d) R. D. Closson, J. P. Napolitino, G. C. Ecke and A. J. Holka, *ibid.*, **22**, 646 (1957).